Phase 1- Determination of the Rates of Conversion of DOE Reprocessed Wastes into Zeolitic Waste Forms

DOE Project: DE-FG07-98ID13649

Principal Investigator; Barry E. Scheetz, The Pennsylvania State University
Co-Principal Investigator: Michael W. Grutzeck**,** The Pennsylvania State University

Report Period: July 1, 1998 -- June 30, 1999

The objective of the current research program was to determine the rates of formation of various hydroceramic waste forms specifically formulated for INEEL calcines. Normally a hydroceramic is formed from a paste-like mixture of a pozzolan[1] such as Class F fly ash or metakaolinite and concentrated sodium hydroxide solution (Palomo and Glasser, 1992; Palomo et al., 1999 a, b). The reaction is rapid and the mechanical properties are more than adequate for making a structural material. In this instance however, other properties such as leachability were more important to program goals than mechanical properties. As a result modifications to formulations had to be made to maximize chemical durability. Up to100 pozzolans were tested as potential ingredients. This was accomplished by mixing various combinations of starting materials with/without INNEL calcines, curing them at 200°C for a few hours and then testing their leachability using conductivity and PCT tests. At this point, a formulation has been chosen and work continues on INNEL site-specific solidification tests.

A major obstacle encountered during this reporting period had to do with turn over of personnel. The program was designed to support a graduate student. The student selected was late in joining the research group and dropped out of program prematurely. Our problem of replacing the student has been compounded because, at this time in the midst of the semester, all students are committed. We are currently searching for a replacement.

---

[1] A pozzolan is defined as any reactive silicate and/or aluminosilicate material (natural or man made) that is able to react with $Ca(OH)_2$ to form a cementitious phase called calcium silicate hydrate. Pozzolans are traditionally added to Portland cement to improve its properties. They react with the excess $Ca(OH)_2$ produced by the hydration reaction and in this way provide an inexpensive but effective means of increasing strength without increasing cost.

Despite these hurdles, excellent progress has been made in the program and it is the opinion of this research team that the ultimate objectives of the program can be achieved. The research activities that were completed under this program have resulted in the publication of two peer-reviewed manuscripts resulting from the two oral presentations that initiated their writing.

Publications Resulting from Talks at National Meetings:

Siemer, D.D., M.L.D. Gougar, M.W. Grutzeck, D.M. Roy and B.E. Scheetz, "Preliminary Formulation Studies for a 'Hydroceramic Alternative Wasteform for INEEL HLW," American Nuclear Society (in press).

Darryl. D. Siemer, Michael W. Grutzeck, and Barry. E. Scheetz, "Comparison of Materials for Making Hydroceramic Waste Forms" American Ceramic *Society (in press).*

Objective:

Review a suite of commercially available aluminosilicate pozzalons and select the most appropriate ones for inclusion in the hydroceramic waste form development portion of this study.

Accomplishments:

The demand for Portland cement across the United States has prompted the industry to begin to use added natural pozzolans as a means of increasing production without adding kiln capacity. As a consequence, many new pozzolans have become available and their use has resulted in the production of high quality Portland cements. The initial objective of this program was to establish one or two reference formulations that would serve as our baseline for the study. This aspect of the program took on a much larger importance when an initial survey of available pozzolans revealed the fact that different pozzolans effected the physical and chemical characteristics of the final hydroceramic in radically different ways.

These observations resulted in a more general survey of pozzolans and an initial attempt to evaluate the effect of mixing pozzolans in order to control and optimize bulk chemistry related properties. Pozzolans evaluated included both natural and industrial by-product materials such as: metakaolin, metakaolin/opal natural mixture, bentonite, finely ground quartz, fly ashes including several examples of eastern and western Class F and a Class C, industrially prepared silica fume, ground recycled glass cullet, finely divided quartz in the form of silica flour, and alumina in the form of boehmite and an industrially available amorphous alumina.

Approach to Solidification with Alkali-Activated Hydroceramics:

The simplest and most cost-effective approach to creating a stable, top-of-the-line waste form is solidification with alkali-activated pozzolans such as metakaolinite and Class F fly ash. Hydroceramics show a great deal of promise. Processing operations are simple and straightforward. Additionally if the need arises, hydroceramics can be HIP treated to form a vitreous product. Major processing stages are listed below:

1) Any existing liquid wastes such as ICPP (Idaho Chemical Processing Plant) wastes should be denitrated by sugar calcining.

2) All calcined products can then be combined with caustic (typically NaOH) and aluminosilicates (metakaolinite and or fly ash) in the proper proportions to produce a thick paste.

3) The resulting paste can then be placed in sealed stainless steel canisters where it can cure under autogenous pressure at temperatures ranging from 150°C to 200°C. Heat is supplied by radioactive decay and external sources (room-sized curing chamber). The ceramic-like product thus produced resembles natural zeolitic mineral assemblages. Thus these materials have been termed hydroceramics.

4) If deemed necessary, residual pore-water may subsequently be driven out of the cured product by autoclaving it under the FUETAP (Formed Under Elevated Temperatures and Pressures) process. This additional process would be undertaken to reduce gross leach rates and to ensure the durability of the hydroceramic product.

General Observations Resulting from Screening Tests

Silica fume does not work well in the grout mixtures because it appears not to be completely oxidized. A huge amount of gas, probably hydrogen, was generated during the curing stages. The silica fume also has an extremely high water demand making low strength, low density products.

Rhone Poulenc amorphous alumina (RPAA) is a very useful additive. This additive increases the reactive alumina content of grouts without adding too much water. When *RPAA is combined with silica flour* it makes a very slow-setting grout that sets into a reasonably hard and dense waste form upon autoclaving. This product may be very useful in situations where waste components might cause flash-set problems.

Silica flour is a good additive, because it is dense, easy to use, and easy to mix. Under autoclaving conditions, silica flour sufficiently reacts to be a useful silica source for hydroceramics.

Calcined high-silica clay pozzolans had a much too high water demand. They were also too reactive to use with simulants that contained large amounts of free hydroxide. Flash-set would be a definite problem if the real radwaste contained many readily available divalent metals such as calcium salts.

Montour fly ash (eastern Class F) appears to be a fairly good additive as well. Its bulk chemical analysis is similar to Ashgrove's Troy Clay pozzolan, but with a lesser water demand. Montour fly ash makes less leachable products than the *Wyoming Jim Bridger Plant flyash (western Class F).* On a side note, the waste loading for the Jim Bridger flyash was a bit extreme since the alkali/alumina ratio of the grout was ~0.95. This was due to the fact that the Jim Bridger fly ash contained only 20% alumina versus the 29% alumina in the Montour fly ash.

As is the case with most of the pozzolans, performance is significantly improved by the addition of RPAA. High waste loading is good. The overall performance of these materials in terms of percentages and absolute amounts of nitrate, sodium, and cesium leached under PCT screening test is better when the atom ratios of alkali to alumina to silica approximates 1:1:1. When the silica to alumina have higher proportions than 1:1, the performance is, in general, not as good.

Mixes of moderate alumina pozzolans such as the Montour flyash added to the (RPAA) approximate the composition of metakaolinite very well. Such mixtures work better than just using the pure metakaolinite by itself. The final RPAA products tend to be denser, stronger, and less leachable except where the nitrate is concerned.

In contrast to the conclusions drawn by the Hanford Clay Researchers back in the 1970's, *bentonite* does not make a good additive. While the final leachability of the hydroceramic products made with mixes of bentonite and RPAA is good, it causes troublesome swelling problems during the curing stage. Plus, the finished products have poor physical strengths and are very porous in appearance.

Our recipes of choice are as follows:

INGREDIENTS OF HYDROCERAMIC*	% Na Leached	% NO_3 Leached	% Cs Leached
21 Parts metakaolinite made from Troy clay, 4 Parts Rhone Poulenc Al_2O_3, 13M NaOH and water.	3.6	4.9	0.10
25 parts metakaolinite made from Troy clay, 13 M NaOH and water.	3.9	18.	0.07

*These starting materials were mixed with existing INNEL calcines and cured at 200°C for 3-8 hours. They were then tested using PCT protocol-they were leached for 35 hours in DI water prior to testing.

References:

A. Palomo and F.P. Glasser, "Chemically-Bonded Cementitious Material based upon Metakaolin," Br. Ceram. Trans. J. 91, 107-112 (1992).

A Palomo, M.W. Grutzeck and M.T. Blanco-Varela, "Alkali Activated Fly Ashes: A Cement for the Future," Submitted to Cement Concrete Research (1999a).

A Palomo, M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez and M.W. Grutzeck, "Chemical Stability of Cementitious Materials Based on Metakaolin," Submitted to Cement Concrete Research (1999b).